

Correlated reorientations in $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ single crystals

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Abstract. Single crystals of aluminium ammonium alum $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ were investigated using dielectric spectroscopy in the frequency range 1 kHz to 1 GHz. On approaching the ferroelectric transition at 58 K from above, a monodispersive polar mode is observed to slow down. The relaxation data can be described in terms of a pure Arrhenius law. The analysis of the dielectric loss reveals that in the paraelectric phase the static susceptibility cannot be described by a single Curie–Weiss law. The thermal variations of the Curie constant indicate that the dipolar correlations of the ammonium ions increase as the temperature is lowered.

1. Introduction

The alums with the general formula $\text{M}^+\text{M}^{3+}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, with M^+ being a monovalent ion or group such as K^+ , NH_4^+ , CH_3NH_3^+ and M^{3+} representing a trivalent ion such as Al, Fe, Cr, etc, are a family of compounds which is well suited to study the mechanisms leading to ferroelectricity [1]. Some time ago electrically ordered states were reported for double salts like the $\text{CH}_3\text{NH}_3\text{Al}$ -alum [2] and the NH_4Fe -alum [1]. However, only recently Sekine *et al* have demonstrated that on cooling, a paraelectric to ferroelectric transition takes place at $T_C = 58$ K in $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (ammonium aluminium sulphate dodecahydrate; AASD) by measuring the spontaneous and reversible polarisation below this temperature [3].

Structural details of AASD have been reported for the high temperature phase (space group $\text{Pa}\bar{3}$) only [4]. Within this cubic phase, one nitrogen-hydrogen axis of the ammonium ion is pointing along one [111] direction [5]. The reorientation of the NH_4^+ ion into an opposite direction requires only a 90° rotation around a twofold axis. This motion is accompanied by a translational shift of the nitrogen of about 0.1 \AA along the [111] direction [5]. The small off-centre shift gives rise to an electric dipole moment. The dynamics of the ammonium ions have been studied by dielectric, ultrasonic and magnetic resonance techniques. The relaxation times have been deduced from dielectric [6–8] or elastic [9] absorption maxima, from nuclear spin lattice magnetisation recovery

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times [5] or from the linewidths of the paramagnetic resonance of Cr^{3+} diluted in ammonium aluminium alum [10]. They all agree with each other, within experimental errors, over many decades in frequency. Such a unique description of molecular motion is seldom possible in ionic solids [11] and that makes this model crystal attractive for further studies.

In particular we are interested in the processes which trigger the ferroelectric transition. Unfortunately, information about the susceptibility χ_s associated with the order parameter, i.e. χ_s as measured along [111], is still missing. The complex dielectric constants of powdered samples [6, 7] or single crystals oriented along [100] [3] have only been reported so far. On the other hand, the susceptibility of the closely related alum $\text{CH}_3\text{NH}_3\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (MASD) is known. Here, χ_s deviates significantly from a simple Curie–Weiss law [1, 2]. This experimental result is in accord with calculations based on a modified pseudo-spin model [12].

One purpose of the present investigation is to detect whether deviations from a single Curie–Weiss law also show up in the paraelectric phase of AASD, as was suggested by Chaudhury *et al* [12]. Therefore the complex dielectric constant ε has been determined along the [111] direction (as opposed to the work of Sekine *et al* [3] who measured it along [100]). In order to obtain the static susceptibility of AASD over a large temperature range, the dielectric loss has been measured for more than 40 frequencies in between 1 kHz and 1 GHz, i.e. a range of six decades in frequency. The paper is organised as follows: first, some experimental details are given; then, the results from our dielectric investigation are presented and analysed in terms of the Debye relaxator model; and finally, we compare the relaxation times from this study with those of other authors and discuss the temperature dependence of the static susceptibility of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

2. Experimental details

A single crystal of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was grown from the saturated aqueous solution of the salt. Crystal plates with dimensions of roughly $3 \times 2 \times 1 \text{ mm}^3$ were cut from the optically clear parts of the crystal. Since the sample turned white when subjected to vacuum, an evaporation using gold electrodes was not possible and so in our experiments, the electrodes were painted with silver paste. However, this led to a relatively large uncertainty in the geometric capacitance of the specimen. Therefore the permittivity data are only being reported in normalised form (with respect to its low temperature value ε_0) and the dielectric loss and static susceptibility are shown in arbitrary units. The dielectric measurements were carried out using the impedance analysers HP4192 (in the range from 10^3 to 10^7 Hz) and HP4191 (in the range from 10^6 to 10^9 Hz). The technique for experiments using the latter instrument is described elsewhere [13]. The sample temperature was controlled with an accuracy of better than 0.1 K from 60 to 300 K.

3. Results and discussion

In figure 1 the real part of the dielectric permittivity ε' of AASD is shown as a function of temperature for several radio-frequencies. At temperatures above the dispersion step the permittivity $\varepsilon'(T)$ decreases monotonically with increasing temperature. On cooling, ε' becomes frequency dependent and finally drops to its low temperature value ε_0 . These

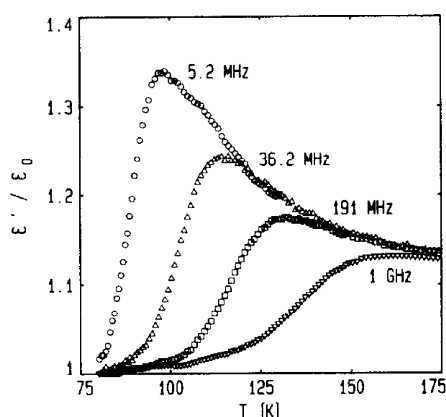


Figure 1. Temperature dependent dielectric constants of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for several radio-frequencies. The data is normalised to the low temperature permittivity ϵ_0 .

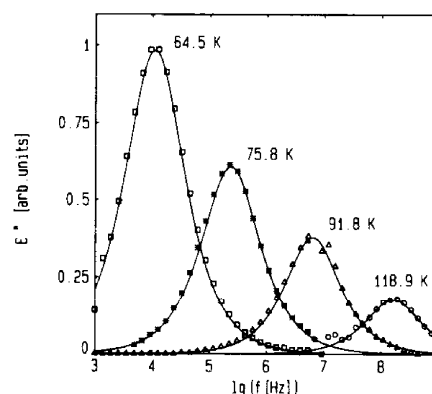


Figure 2. Dielectric loss spectra $\epsilon''(\omega)$ for different temperatures. The solid lines were calculated using the Debye relaxator model (1) with the relaxation times and the coefficient A as free parameters. The time constants are given by (2) and the coefficient A is presented in figure 4.

observations resemble those made on powdered samples [6] or on single crystals at lower frequencies [3].

Results from our dielectric loss measurements in a broad spectral range are presented in figure 2. Well defined Debye peaks are observed. These shift to lower frequencies $\omega = 2\pi f$ with decreasing temperatures. The solid lines in figure 2 are the results of least-squares fits using

$$\epsilon''(\omega) = A\omega\tau/(1 + \omega^2\tau^2). \quad (1)$$

The lines are in good agreement with the experimental data. The Debye losses are commonly found in monodispersive dielectrics, i.e. for those which can be characterised by a single relaxation time τ . In ferroelectrics it is generally observed that τ increases when the transition temperature is approached on cooling [14]. This is not only true for the ferroelectrics of the order-disorder type, but also holds for compounds such as BaTiO_3 [15] which are classified conventionally as displacive ferroelectrics. The temperature dependence of the relaxation rates $f = 1/(2\pi\tau)$ of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was deduced from fits of the dielectric loss data using (1). As shown in figure 3, τ can be described by an Arrhenius law

$$\tau = \tau_0 \exp(E/k_B T). \quad (2)$$

Least-squares fits to the relaxation times from the present study yielded the prefactor $\tau_0 = 1.37 \times 10^{-14}$ s and the energy barrier $E/k_B = 1340$ K. Figure 3 shows that our data are in good agreement with results from dielectric measurements on powdered samples and from those obtained by other experimental techniques. Therefore, it is concluded that the barrier against NH_4 displacements along the [111] direction is identical to the barrier against ammonium reorientations. Deviations from thermally activated behaviour close to T_C have been reported by Sekine *et al* [3]. Their results from permittivity measurements along the [100] direction are also shown in figure 3.

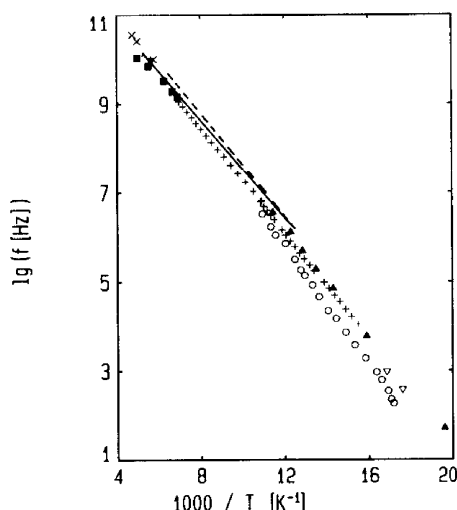


Figure 3. $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$: activation plot. In this representation the Arrhenius law (2) yields a straight line. The relaxation rates $f = 1/(2\pi\tau)$ of this work (+) are compared to those from dielectric measurements on powdered samples (\blacktriangle [6], \blacktriangledown [7], \times [8], ∇ [19]) or other experimental techniques: paramagnetic electron spin resonance (\blacksquare [10]), nuclear magnetic resonance (full curve [5]), ultrasonic investigations (broken curve [9]). Circles represent data by Sekine *et al* [3] who measured the dielectric constants along [100].

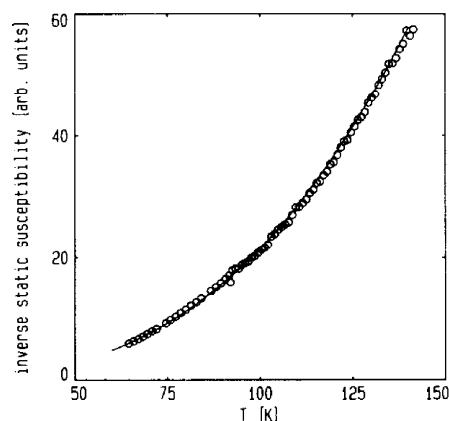


Figure 4. Inverse static susceptibility versus temperature of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ as deduced from the fits to the dielectric loss according to (1). Deviations from a simple Curie–Weiss law $\chi_s^{-1} = (T - T_0)/C$ are obvious. Data for $T \geq 115$ K can be described using a Weiss temperature $T_0 = (85 \pm 3)$ K. The line is calculated using $\chi_s \sim T^{-3}$.

The area under the dielectric loss peaks, presented in figure 2 on a logarithmic frequency scale, strongly increases on cooling. From the Kramers–Kronig relation

$$\chi_s = \frac{1}{2\pi^2} \int_0^\infty \frac{\varepsilon''(\omega)}{\omega} d\omega, \quad (3)$$

it is obvious that the static susceptibility χ_s is proportional to the area under the loss curves and the coefficient A , as defined in (1). The right hand side of (3), i.e. $\varepsilon''(\omega)$, contains contributions only from the orientational polarisation. The calculation of the static susceptibility is therefore free from the assumptions made about the polarisation of the lattice when χ_s is computed from the real part of the dielectric permittivity (as done in [3]). The inverse static susceptibility obtained in this work is shown in figure 4. Deviations from a simple Curie–Weiss law with $1/\chi_s = (T - T_0)/C$ are being observed. Figure 4 shows that the description in terms of this law requires a temperature dependent Curie constant C . At least two different Curie–Weiss laws, one below and one above approximately $T' = 110$ K are needed to describe the temperature dependence of the static susceptibility. From our dielectric experiments the ratio of the Curie constants is estimated to be $C_{T < T'}/C_{T > T'} \approx 2.1$.

We note that Jona and Shirane showed that the description of the susceptibility of MASD over a large temperature range required three different Curie constants [1]. The ratio of the largest to that of the smallest C value was found to be 2.4. On the other hand,

in the vicinity of the ferroelectric transition, a description with a single Curie–Weiss law was demonstrated to be sufficient for AFESD [16].

To explain the susceptibilities in MASD and AFESD, Chaudhury *et al* [12] have extended the pseudo-spin model by taking into account the anharmonic interaction potential between the pseudo-spin waves and the lattice, that is between the (methyl-) ammonium ion and the optical vibrations. They deduced an expression for the Curie constant, $C \sim (\bar{A}'_0 + B)^{-1}$, which is composed of two terms. The latter is calculated in the harmonic approximation from coefficients such as the spin–spin coupling constants, renormalised proton tunnelling frequencies, etc. \bar{A}'_0 is the anharmonicity parameter of the interaction potential. Within the framework of this model, the anharmonicity term was found to be almost negligible for AFESD [12]. But for MASD a large and temperature dependent \bar{A}'_0 was used to explain the variation of the Curie constant [12]. It was argued by Chaudhury *et al* that the static susceptibility of AASD should also exhibit deviations from a simple Curie–Weiss law. However, a quantitative description in terms of their pseudo-spin model requires a number of assumptions to be made about several factors involved in coefficient B .

An interpretation of the temperature variations of the Curie constant, which is free from such assumptions, can be given in terms of super-paraelectricity. The magnetic analogue of this phenomenon is well known [17]. At high temperatures the dipoles are assumed to reorientate freely and the Curie constant is given by $C = n\mu^2/(3k_B)$. Here n and μ denote the density and the dipole moment of the relaxing species. If a number of ξ dipoles reorientate cooperatively, then the Curie constant increases according to $C' = (n/\xi)(\xi\mu)^2/(3k_B) = \xi C$. Such an increase is indeed observed in AASD (figure 4). This suggests that variations of dipolar correlations are responsible for the deviations from a simple Curie–Weiss law. The experimental results indicate a continuous increase of ξ as the ferroelectric transition is approached from high temperatures. Interestingly, marked correlation effects are seen already at $T' \approx 110$ K, i.e. at $T \approx 2 T_C$.

Finally, it should be mentioned that the static susceptibility can also be parametrised using $\chi_s \sim (T - T_0)^{-\gamma}$ with $\gamma = 3$. However, an interpretation in terms of critical phenomena is not straightforward since this fit (shown as a line in figure 4) yielded $T_0 = 0$ K. Moreover, the experimental exponent is considerably larger than predicted by the multi-state Potts model or even by the spherical model. These models give at the most an exponent of $\gamma = 2$ [18].

4. Summary

We have measured the complex dielectric constant of a single crystal of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in the frequency range between 1 kHz and 1 GHz and for temperatures $60 \text{ K} < T < 300 \text{ K}$. It has been shown that the slowing down of dipolar active ammonium reorientations can be described by a monodispersive and a thermally activated relaxation mode. From an analysis of the dielectric loss spectra, the static susceptibility χ_s of the dipolar modes was determined over a large temperature range. It was not possible to describe χ_s by a single Curie–Weiss law. The Curie constant was shown to increase when approaching the ferroelectric transition from high temperatures. This was interpreted as being indicative for increasing dipolar correlations.

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